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RAMAN SPECTRA OF SOLUTIONS OF ETHYLENE DICHLORIDE, ETHYLENE DIBROMIDE AND ETHYLENE CHLORHYDRIN AT LOW TEMPERATURES*

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(*Received, January 5*, 1959)

ABSTRACT. The Raman spectra of 25% solutions in ethyl alcohol of ethylene dichloride at 30°C, – 60°C and –180°C, of ethylene dibromide at 30°C and – 5°C and of ethylene chlorhydrin at 30°C – 80°C, and –180°C have been studied and the ratio of intensities of the lines 654 cm^{-1} and 755 cm^{-1} in the first case, 551 cm^{-1} and 660 cm^{-1} in the second case and 662 cm^{-1} and 750 cm^{-1} in the third case has been determined quantitatively. It has been observed that in the case of solutions of ethylene dichloride and ethylene dibromide the number of gauche type of molecules tends to diminish at lower temperatures while in the case of the pure liquids the number diminishes with the rise of temperature. In the case of solution of ethylene chlorhydrin the change in the ratio of intensity of the lines mentioned above is smaller and the ratio increases at lower temperatures. It is pointed out that these results cannot be explained on Wada's (1954) theory and that the hypothesis of virtual linkages between the hydrogen atoms of the OH groups of neighbouring solvent molecules and the chlorine and bromine atoms of the molecules of the liquids can explain the results satisfactorily

INTRODUCTION

The abrupt change in the ratio of intensity of the two Raman lines 654 cm^{-1} and 755 cm^{-1} of ethylene dichloride which takes place when the liquid at 25°C is transformed into vapour at 170°C was first demonstrated by Morino *et al* (1941). Watanabe *et al* (1942) explained the results by assuming that the energy-difference of the two rotational isomers, namely *trans* and *gauche*, of ethylene dichloride increases with the change from the liquid to the vapour state. The present author (1953), however, studied the Raman spectrum of gaseous ethylene dichloride at 135°C and measured the ratio of intensity of the lines 654 cm^{-1} and 755 cm^{-1} which was found to be 1 : 4.5, while the value obtained by Watanabe *et al* (1942) at 170°C is 1 : 5. This shows that the ratio does not change very much with the change of temperature of the vapour from 135°C to 170°C. Watanabe *et al* (1943) tried to explain the change in the energy-difference due to the change of state mentioned above by assuming that in the liquid state the gauche molecule acquires an excess of electrostatic energy which is equal

* Communicated by Professor S. C. Sirkar.

to $\mu^2(\epsilon-1)/(2\epsilon+1)a^3$, where ϵ is the dielectric constant, μ the permanent electric moment of the gauche molecule and a is the radius of the cavity of the solute molecule. They showed that the influence of this electrostatic energy would diminish the energy-difference of the two types of molecules to a very small value in the liquid state.

If the liquid were dissolved in a solvent having non-polar molecules, the dielectric constant of the medium would be expected to be much lower than that of the pure liquid and the energy-difference of the trans and gauche molecules would be larger than that in the pure liquid. When, however, the solution is further diluted the dielectric constant of the medium is not likely to change appreciably and hence there should not be any appreciable change in the energy-difference of the two types of molecules. Banerjee (1954), however, observed that the ratio of intensity of the lines 654 cm^{-1} and 755 cm^{-1} of ethylene dichloride diminishes when the liquid is dissolved in heptane and cyclohexane to make a 65% solution and that the ratio diminishes further when the concentration is diminished to 35% in each case. Very recently, the present author (1958) studied the infra-red absorption spectra of solutions of ethylene dichloride in carbon tetrachloride, heptane and methyl cyclohexane of different concentrations and observed that the ratio of the integrated intensities of the absorption peaks 1297 cm^{-1} and 1236 cm^{-1} in the case of 20% solutions in heptane and methyl cyclohexane is less than that for the pure liquid and that the ratio diminishes further when the strength of the solution is diminished to 3%. In the case of solution in carbon tetrachloride the changes in the ratio mentioned above are much smaller. This indicates that probably the changes in the energy-difference brought about by the electrostatic field in the solution are not responsible for the observed change in the intensities of the two lines.

The hypothesis put forward by Watanabe *et al* (1943) mentioned above would, however, be tested more conclusively by changing the temperature of the solution and finding out whether the relative intensities of the two lines change in accordance with the energy-differences derived from their hypothesis. With this object in view the Raman spectra of solutions of ethylene dichloride, ethylene chlorhydrin and ethylene dibromide in ethyl alcohol at different temperatures below 30°C and also of the first two solutions at −180°C have been investigated and the relative intensities of the lines 654 cm^{-1} and 755 cm^{-1} in the case of ethylene dichloride, 662 cm^{-1} and 750 cm^{-1} in the case of ethylene chlorhydrin and 551 cm^{-1} and 660 cm^{-1} in the case of ethylene dibromide have been measured. These results have been discussed in the present paper in the light of the hypothesis put forward by Watanabe *et al* (1943).

EXPERIMENTAL

Dehydrated ethyl alcohol was chosen as the solvent and was distilled several times under reduced pressure before being used in the solutions. The experimental

arrangement used to record the Raman spectra of the solutions at low temperatures is shown in figure 1. The scattered light was reflected by the right angled prism, P, attached at the bottom of the Dewar vessel and was focussed on the slit of the spectrograph. The container of the liquid, C, was placed inside the Dewar vessel dipped in ethyl alcohol which was then gradually cooled by adding small quantities of liquid oxygen to it until the required temperature was attained. Liquid oxygen had to be added frequently to keep the temperature fairly constant. The temperature was read with the pentane thermometer, T.

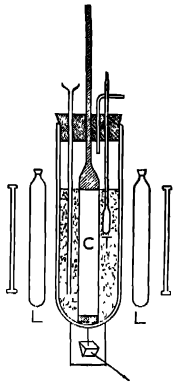


Fig. 1.

The Raman spectra of 25% solution of ethylene dichloride, ethylene dibromide and ethylene chlorhydrin at – 60°C, – 5°C and – 80°C respectively were photographed using this arrangement. The Raman spectra of the last two solutions in the frozen state at – 180°C were also photographed by keeping the sample tube immersed in liquid oxygen.

A Fuess glass spectrograph having a dispersion of about 11 A.U. per mm in the 4046 A.U. region was used to record the spectra. Microphotometric records of the lines were taken with a Kipp and Zonen type self-recording microphotometer. Using blackening log-intensity curves drawn with the help of intensity marks taken with known slit-widths and continuous radiation the intensities of the lines mentioned above of ethylene dichloride, ethylene dibromide and ethylene chlorhydrin in the pure state and in solutions at different temperatures, were measured quantitatively.

RESULTS AND DISCUSSION

Microphotometric records of the lines 654 cm^{-1} and 755 cm^{-1} due to pure ethylene dichloride at 30°C and its solution in ethyl alcohol at 30°C and – 60°C,

551 cm^{-1} and 660 cm^{-1} due to pure ethylene dibromide at 30°C and its solution at 30°C and – 5°C, 662 cm^{-1} and 750 cm^{-1} due to pure ethylene chlorhydrin at 30°C and its solution at 30°C and – 80°C are reproduced in figures 2, 3 and 4 respectively. The values of the ratio of intensities of the two lines observed in each case mentioned above are given in Tables I, II and III.

TABLE I

Raman spectra of ethylene dichloride
Value of I_{654}/I_{755}

Pure liquid		Solution in EtOH		
at 30°C (Watanabe *et al* 1942)	at -25°C	at 30°C	at – 60°C	at –180°C
1 : 1.8	1 : 1.5	1 : 1.3	1 : 1.5	0 : 3

TABLE II

Raman spectra of ethylene dibromide
Value of I_{551}/I_{660}

Pure liquid at 30°C	Solution in EtOH	
	at 30°C	at – 5°C
1 : 7	1 : 6	1 : 6.2

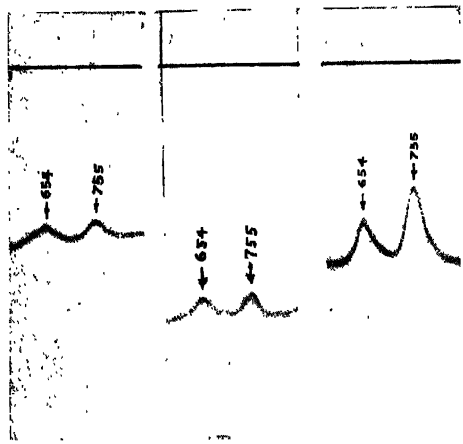
TABLE III

Raman spectra of ethylene chlorhydrin
Value of I_{662}/I_{750}

Pure liquid at 30°C	Solution in EtOH		
	at 30°C	at – 80°C	at –180°C
2 · 1	2.2 : 1	2.5 : 1	4 : 1

(i) *Ethylene dichloride*

It can be seen from Table I and figure 2 that the ratio of the intensity of the lines 654 cm^{-1} and 755 cm^{-1} of ethylene dichloride changes from 1 : 1.8 to 1 : 1.3 when the liquid is dissolved in ethyl alcohol to make a 25% solution and that the ratio becomes 1 : 1.5 when the solution is cooled down to – 60°C. Moreover, when the solution is solidified and cooled to –180°C the line 654 cm^{-1} disappears and the line 755 cm^{-1} appears with its intensity relative to that of the line 300 cm^{-1} increased to about double the value for the liquid state. These results, therefore, clearly show that if the line 654 cm^{-1} be assigned to the gauche configuration, the number of such molecules increases when the liquid is dissolved



(*a*) (*b*) (*c*)

Fig. 2 Microphotometric records of the Raman spectra of ethylene dichloride.
(*a*) Solution at –60°C.
(*b*) Solution at 30°C.
(*c*) Pure liquid at 30°C.

in alcohol and that the number then diminishes when the temperature of the solution is lowered to – 60°C. On the other hand Watanabe *et al* (1942) have shown that in the case of pure ethylene dichloride the ratio I_{660}/I_{768} increases from 1 : 2 to 1 : 1.5 when the temperature of the liquid is lowered from 150°C to –25°C. Wada (1954) suggested that the energy of the gauche molecule is lowered in the state of aggregation owing to the influence of the field due to the surrounding permanent dipoles on the permanent moment of the molecules. According to his calculations in the pure liquid both the gauche and the trans molecules are of the same energy, while in solution in methyl alcohol the energy

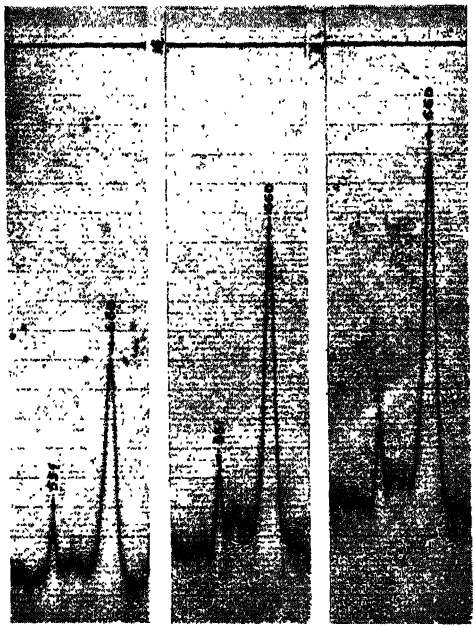
of the gauche molecule is lower than that of the trans molecule by 260 cal/mole. Hence the number of gauche molecules would increase at lower temperatures in solution in methyl alcohol and similar results would be expected in the case of solution in ethyl alcohol also. Actually, however, it is observed that in the case of solution in ethyl alcohol the number of gauche molecules increases with rise of temperature, while in the case of pure liquid the number diminishes with the rise of temperature. Thus the results for the solution and the liquid at low temperatures are not in agreement with the predictions of Wada's theory.

From the argument stated above, it is clear that the ratio of population of the two types of molecules is not determined by the energy-difference of the trans and gauche molecules in the liquid, as postulated by Watanabe *et al* (1942). On the other hand, it can be explained by arguing that the OH groups of the alcohol molecules are linked to one of the chlorine atoms of ethylene dichloride and the random distribution of the alcohol molecules and their restricted freedom of motion about the C-C bond produce the change from the trans to the gauche configuration When, however, the solution is cooled to a very low temperature the freedom of movement of the solvent molecules decreases and both the chlorine atoms of the ethylene dichloride molecules form virtual linkage with hydrogen atoms of the neighbouring molecules and ultimately the two virtual linkages come in the same plane to produce the trans configuration in the solid state.

(ii) *Ethylene dibromide*

The results given in Table II and the microphotometric records reproduced in figure 3 show that the ratio of the intensity I_{651}/I_{660} slightly increases when ethylene dibromide is dissolved in ethyl alcohol and the ratio tends to diminish slowly when the solution is cooled down to $-5°C$. So, the changes with lowering of temperature of the solution are similar to those observed in the case of ethylene dichloride.

According to the calculations made by Wada (1954) the decrease of energy-difference between gauche and trans configuration with liquefaction of the vapour and dissolution in methyl alcohol would be respectively 1270 and 1530 cal/mole in the case of ethylene dichloride but the values are 900 and 1170 cal/mole in the case of ethylene dibromide. So, the gauche molecules of ethylene dibromide should have energy higher than that of the trans molecules in the solution, but in the case of ethylene dichloride the reverse is true. The changes in the ratio of the numbers of the two types of molecules with change of temperature are, however, similar in both the cases. Hence the cause of this change is different from the energy-difference of the two types of molecules in solution and evidently the formation of virtual linkage mentioned above takes place in both the cases. The results of investigation on the infra-red absorption spectra of ethylene dichloride in different solvents reported earlier (Mazumder, 1958) support such a conclusion.



(*a*) (*b*) (*c*)

Fig. 3. Microphotometric records of the Raman spectra of ethylene dibromide.

(*a*) Solution at – 5°C.

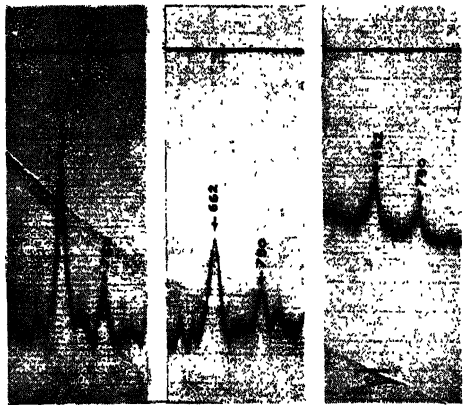
(*b*) Solution at 30°C.

(*c*) Pure liquid at 30°C.

(iii) *Ethylene chlorhydrin*

It can be seen from Table III and figure 4 that the ratio of the lines 622 cm^{-1} and 750 cm^{-1} becomes 2.2 : 1 when ethylene chlorhydrin is dissolved in ethyl alcohol and the ratio increases slightly to 2.5 : 1 when the solution is cooled down to – 80°C. In the case of pure liquid the ratio is 2 : 1. So the ratio increases very slightly when the liquid is dissolved in alcohol. Mizushima *et al* (1940), however, observed a larger change in the ratio of intensity of the two lines when they dissolved the liquid in water. Evidently, the greater number of OH groups around each molecule in the solution is responsible for the difference. Mizushima *et al* (1939) had earlier studied the infra-red absorption due to second harmonic

of the OH vibration and concluded that in the vapour there are two configurations of the molecules, one formed by weak attraction between the chlorine atoms and the hydrogen atoms of the OH group in the same molecule and the other the trans configuration. In the liquid they observed only the presence of the former configuration. In the Raman spectrum of the liquid also there is no line in the vicinity of 3350 cm^{-1} due to the OH valence oscillation. Hence it is evident that most of the molecules in the liquid are associated with each other through



(*a*) (*b*) (*c*)

Fig. 4. Microphotometric records of the spectra of ethylene chlorhydrin.

(*a*) Solution at − 80°C.

(*b*) Solution at 30°C.

(*c*) Pure liquid at 30°C

hydrogen-chlorine virtual linkages and this is responsible for the larger intensity of the line 662 cm^{-1} in this case than in the case of ethylene dichloride and ethylene dibromide. In the vapour this line is very weak (Mazumder, 1955) and therefore most of the molecules are single. Calculation of frequencies of the modes of vibration of the molecules carried out by Mizushima *et al* (1951) shows that the line 750 cm^{-1} is due to the trans configuration. Hence the other configuration is formed by association of single molecules and has energy lower than that of the trans configuration as assumed by Mizushima *et al*. This explains the wide discrepancies between the values of energy-difference calculated by them and those reported by Zumwalt and Badger (1940). As the association is rather strong and most of the molecules are associated in the liquid, in the solution in alcohol not much change in the number of associated molecules occurs.

When, however, the solution is cooled to – 80°C the number of such molecules increases and when the solution is frozen all the molecules become associated and the line 750 cm^{-1} disappears. When the pure liquid is frozen the line 750 cm^{-1} appears with a very feeble intensity (Bishui, 1948) which shows that only a few percentage of the molecules are of the trans configuration in the solid state.

ACKNOWLEDGMENT

The author is indebted to Professor S. C. Sirkar, D.Sc., F.N.I., for his kind interest and helpful guidance throughout the progress of the work.

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